

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY


(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

REC'D 28 OCT 2005

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Applicant's or agent's file reference 6166		FOR FURTHER ACTION		See Form PCT/PEA/416
International application No. PCT/IB2004/002285		International filing date (day/month/year) 12.07.2004	Priority date (day/month/year) 18.07.2003	
International Patent Classification (IPC) or national classification and IPC C22B13/04, H01M10/54				
Applicant KANDY S. A. et al.				
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau) a total of 4 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>				
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input checked="" type="checkbox"/> Box No. VIII Certain observations on the international application</p>				
Date of submission of the demand 03.02.2005		Date of completion of this report 27.10.2005		
Name and mailing address of the International preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized Officer Bjoerk, P Telephone No. +49 89 2399-8452		



**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/IB2004/002285

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

Description, Pages

1-6	as originally filed
7, 8	filed with telefax on 23.09.2005

Claims, Numbers

1-8	filed with telefax on 23.09.2005
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- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/B2004/002285

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-8
	No: Claims	
Inventive step (IS)	Yes: Claims	1-8
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-8
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Section V

1. The present application relates to a desulphating process of lead-acid battery residues such as electrode slime. In the restricted claim 1, the residues are treated with an aqueous solution containing alkali carbonates and alkali hydroxides the solid phase of the resulting suspension is subjected to shear and compression forces exerted by brushing, scraping and compressing mechanical means.

A near to complete desulphating can thereby be achieved.

Examples of the means used for the shearing and compression are rotating brushes and paddle stirrers according to the description.

The dependent claims relate to process parameters such as the ratio of carbonate and solvent, the ratio of water and suspended solid phase, the duration of the desulphating and the process temperature. Claim 8 relate to a pyrometallurgical process for recovering lead from lead-acid batteries comprising the desulphating process of claim 1.

2. Reference is made to the following documents:

D1: US-A-3 883 348

D2: BEGUM D A ET AL: "A STUDY ON THE DISSOLUTION OF LEAD SULPHATE FROM WASTE BATTERIES WITH ETHANOLAMINES" HYDROMETALLURGY, ELSEVIER SCIENTIFIC PUBLISHING CY. AMSTERDAM, NL, vol. 22, no. 1/2, 1 June 1989 (1989-06-01), pages 259-266

D3: US-A-5 690 718

D4: US-A-4 018 567

D1 and D2 disclose processes for removal of sulphur from waste battery material such as lead-acid batteries. D1 uses leaching with an ammonium carbonate solution (col.7, l.28-45) and D2 dissolution with ethanolamines followed by stripping with either sodium carbonate or sodium hydrogen carbonate (p.260, "Experimental").

D3 discloses a battery paste recycling process whereby desulphating is performed with a solution of sodium carbonate. Example 2 uses a magnetic stirrer or a laboratory blender and teaches that other well known methods of agitation could be used such as paddle mixing and air-lift mixing (col.10, l.56-66).

D4 discloses an apparatus for separating the constituents of lead-acid batteries, said apparatus comprising a drum containing grinding balls. Battery residues, sodium carbonate and water are fed into the drum which is subsequently rotated. The grinding action serves to fragmentize the batteries and to transpose the lead sulphate particles into lead carbonate (claim 1).

3. None of D1 to D4 discloses a treatment with a solution containing both alkali carbonates and alkali hydroxides. Such a combination is also not hinted at in the available prior art.

Novelty and inventive step can therefore be recognised for the claimed subject matter (Art.33(2) and (3) PCT).

Section VIII

1. The two-part form for the present process claims is not seen as appropriate (see PCT Guidelines 5.05-5.08).
2. The terms in brackets in claim 1 are not seen as having any limiting effect on the scope of the claim (see PCT Guidelines 5.40).
3. Claim 7 does not indicate the unit for the temperature (Art.6 PCT).
4. The restriction made to the process of claim 1 is allowable in view of Art.34(2)(b) PCT. The passage on page 6, lines 12-26 has however not been put in line with this amendment, contrary to Art.6 PCT, last sentence.

Claims

1. Process for desulphating a solid mixture resulting from the breaking up of lead-acid batteries, comprising electrode slime residues containing lead compounds belonging to the groups comprising oxides, oxysulphates (lanarkite) and sulphates, characterised in that said lead compounds are put in contact with a aqueous solution containing alkali carbonate (sodium or potassium carbonate) in the stoichiometric quantity sufficient for sulphate concentrations present in the electrode slime, plus an excess of between 0,01% and 10%, and alkali (sodium, potassium) hydroxides which dissolve lanarkite in a molar ration of carbonate to alkali of between 1 and 2,75, in which the said lead compounds are suspended, the solid phase of the suspension being subjected to the fragmenting action of shear and compression forces exerted by brushing, scraping and compressing mechanical means.
2. Desulphating process according to claim 1, characterised in that the carbonate/solvent molar ratio is less than 1.
3. Desulphating process according to claim 1, characterised in that the ratio by weight between water and the suspended solid phase lies between 0.6 and 5, preferably between 0.7 and 1.2.
4. Desulphating process according to claim 1, characterised in that the sodium carbonate in the said solution is in excess with respect to the stoichiometric quantity necessary for the quantity of sulphate present up to a maximum of 10 percentage points and the carbonate/alkali molar ratio may be between 1 and 2.75.

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5. Desulphating process according to claim 1, characterised in that the contact time necessary for almost total conversion of the lead sulphate to lead carbonate is between 30 and 90 minutes.
6. Desulphating process according to any of the preceding claims, characterised in that it takes place at a temperature between ambient temperature and the boiling point of the solution.
7. Process according to claim 6, characterised in that it takes place at a temperature of between 60 and 100°.
8. Pyrometallurgical process for the recovery of lead from lead-acid battery electrode slime residues without the use of iron in the charge, characterised in that the said residues are first desulphated in accordance with the procedure according to claim 1 until they are substantially free of lead sulphate.

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brushes brushing against the inside walls of the reactor. At the end of the reaction the solid part of the suspension was separated out from the suspension and on analysis was found to have a total sulphur content of less than 0.06%.

The same desulphating experiment was repeated with sufficient quantities to charge an industrial furnace and a charge of 14 tons of desulphated slime with a residual moisture content of 30%, to which 0.5 tons of carbon, 0.2 tons of sodium carbonate and 0.1 tons of glass were added, produced a yield of 7,320 kg of lead metal accompanied by approximately 0.4 tons of slag with a lead content of less than 10%.

Example 2

100 kg of electrode slime was charged into a cylindrical reactor with a paddle stirrer and suspended in a solution comprising 100 kg of water, 24 kg of 99% pure sodium carbonate and 8 kg of 99.5% pure sodium hydroxide. The suspension was heated to a temperature of 70°C and held at that temperature for 90 minutes. Again in this case the grinding action was applied throughout the duration of the test. At the end of the reaction the solid part of the suspension was separated out from the and on analysis was found to have a total sulphur content of less than 0.04%.

Example 3

~~100 kg of electrode slime were charged into the same cylindrical reactor as in example no. 1 and suspended in a solution comprising 100 kg of water, 24 kg of 99% pure sodium carbonate and 5 kg of urea. The suspension was heated to a temperature of 75°C and held at that temperature for 90 minutes. Again in this case the grinding action was maintained throughout the duration of the test. At the end of the reaction the solid part~~

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~~of the suspension was separated out and on analysis was found to have a total sulphur content of less than 0.09%.~~

Example 4

~~100 kg of electrode slime was charged into the same cylindrical reactor as in example no. 1 and suspended in a solution comprising 100 kg of water, 24 kg of 99% pure sodium carbonate and 6 kg of monoethanolamine. The suspension was heated to a temperature of 70°C and held at that temperature for 90 minutes. Again in this case the grinding action was maintained throughout the duration of the test. At the end of the reaction the solid part of the suspension was separated out and on analysis was found to have a total sulphur content of less than 0.07%.~~

Example 5

~~100 kg of electrode slime was charged into the same cylindrical reactor as in example no. 1 and suspended in a solution comprising 100 kg of water and 22 kg of 99% pure ammonium carbonate. The suspension was heated to a temperature of 70°C and held at that temperature for 90 minutes. Again in this case the grinding action was maintained throughout the duration of the test. At the end of the reaction the solid part of the suspension was separated out and on analysis was found to have a total sulphur content of less than 0.07%. It was not necessary to add solvent of any kind in this case because the ammonium ion $(\text{NH}_4)^+$ has the power of complexing lanarkite.~~

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